Synthesis and Characterization of Metal Nitrides for Atmospheric Pressure Ammonia Production

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Abstract

Ammonia is a key molecule used in many forms of industry. Current production uses the Haber-Bosch process which involves carbon dioxide emissions and a large amount of energy to apply extreme pressures. The proposed method will use solid oxide fuel cell-like reactors with a metal nitride catalyst to produce ammonia from water and nitrogen with the byproduct of oxygen. Investigation of molybdenum nitride and vanadium nitride was conducted in order to determine successful synthesis methods and decomposition temperatures. X-ray diffractometry (XRD) was utilized to determine the structure of the samples and temperature-programmed decomposition (TPD) was utilized to determine the decomposition temperature. Vanadium nitride was successfully produced in a pure form and had a decomposition temperature of 900 °C. Molybdenum Nitride was unable to be synthesized in pure form, but gave TPD results that suggested it may be stable if produced purely enough. Further metal nitrides will be studied and implemented into SOFC-like reactors to determine the effectiveness in producing ammonia in this application.

Introduction

Ammonia is an essential molecule in the production of many products such as fertilizers, household cleaning products, and pharmaceuticals. Currently, ammonia is produced industrially through the Haber-Bosch process. This method converts hydrogen and nitrogen gas into ammonia as shown in equation 1.

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad (1)$$

This reaction occurs under extreme pressures of 50 to 200 bar and high temperatures of 650 to 750 Kelvin in the presence of a catalyst. This process has been undergoing changes since its discovery over 100 years ago [1]. Despite its advancements, the process still requires large pressures that contribute to over 1% of the world's total energy consumption. In addition, the process releases greater than 300 million metric tons of carbon dioxide into the atmosphere per year [2]. Discovering a more sustainable ammonia production method is imperative to the preservation of the environment of our planet.

Previous research on the electro-catalytic production of ammonia has shown that it can be produced through a Mars-van Krevelen mechanism. In this reaction network, the nitrogen ions within the metal nitride reacts to form ammonia and the lost nitrogen is replenished with a stream of nitrogen gas. The study performed a computational screening of metal nitrides capable of electro-catalytically producing ammonia in order to determine the most suited catalysts: vanadium nitride, chromium nitride, niobium nitride, and zirconium nitride [3].

Our proposed method seeks to remove the need for hydrogen gas and high pressures through the electro-catalytic production of ammonia at ambient temperatures. Within a solid oxide fuel cell-like reactor, water and nitrogen will react on the surface of a metal nitride to produce ammonia with the only byproduct of water. While operating at temperatures similar to the Haber-

Bosch process, this method has the advantage of removing the need for hydrogen and energy-intensive pressure application.

Zhao et al. determined the thermal nitridation of the ammonium vanadate to proceed through the reaction network shown by equations 2 through 6. [4]

$$2NH_4VO_3 \rightarrow V_2O_5 + 2NH_3 \uparrow + H_2O \uparrow \quad (2)$$

$$V_2O_5 + C \rightarrow 2VO_2 + CO \uparrow \quad (3)$$

$$9VO_2 + 2C \rightarrow V_5O_9 + V_4O_7 + 2CO \uparrow \quad (4)$$

$$2V_5O_9 + V_4O_7 + 4C \rightarrow 7V_2O_3 + 4CO \uparrow \quad (5)$$

$$V_2O_3 + (5 - 2X)C \rightarrow 2VC_{1-X} + 3CO \uparrow (1 - X = 0.66 - 0.88) \quad (6)$$

$$2VC_{1-X} + N_2 \rightarrow 2VN + 2(1 - X)C \quad (7)$$

After producing a properly mixed powder of carbon black and the ammonium vanadate, the sample can proceed through the reaction network under nitrogen flow at a temperature of 1050 °C. Through a series of reducing steps of the vanadium, it becomes prepared to be nitrided by the nitrogen stream. With the presence of the carbon, the oxygen has something to bond with to leave the vanadium.

Molybdenum was also investigated in another study due to the ability of metallic molybdenum to break apart gaseous nitrogen which is needed in our approach to producing ammonia electro-catalytically [6].

Previous research from the team on iron nitride revealed that it was active in ammonia production but was not stable at temperatures high enough to be implemented into a solid oxide fuel cell system. The material used to separate the anode and cathode compartments of the SOFC-type reactor needs to be cured at 700 °C. Based off prior research, vanadium nitride and

molybdenum nitride were chosen to be studied. Synthesis methods and decomposition temperatures of these metal nitrides will be analyzed to determine their effectiveness in the application of ammonia production via electro-catalysis.

Methodology

In order to synthesize the vanadium nitride and molybdenum nitride, Zhao et al. study's synthesis method was chosen and adapted to be replicated in our laboratory [4]. First, ammonium vanadate and carbon black (1.95:1 ammonium vanadate to carbon black weight ratio) were mixed in de-ionized water at 80 °C for 1 hour. Next, the suspension was dried overnight at 150 °C. The following morning, the dried product was grinded into a fine powder and nitrided with nitrogen in an alumina boat in a tubular furnace at 1,050 °C for 3 hours. Molybdenum nitride was produced using the same method but using a 4.90:1 ammonium heptamolybdate to carbon black weight ratio. In addition, a replication of the molybdenum sample was produced at a nitridation temperature of 950 °C.

X-ray diffraction (XRD) studies for iron nitride (Fe-N), molybdenum nitride (Mo-N) and vanadium nitride (V-N) were performed using a Bruker D8 Advance Diffractometer with a Cu Kα (λ = 1.5046 Å, 40 kV and 40 mA) radiation source under ambient conditions. A step size of 0.014° was used at a dwell time of 0.75 seconds, and spectra were obtained between 2θ angles of 10 to 90°.

Temperature-programmed decomposition (TPD) experiments were conducted in order to determine the decomposition temperature (nitrogen release temperature) of the synthesized nitride materials. Fe-N, V-N, Mo-N synthesized at 1050 °C, and Mo-N synthesized at 950 °C (25 mg of each powder) were first loaded into a quartz reactor tube, and placed inside a tubular

furnace. After 1 hour of reactor flushing using 30 cubic centimeter per minute flow of helium at room temperature, the catalyst bed was heated at 10°C/min under 30 standard cubic centimeter per minute flow of helium to 1000 °C and held for 1 hour. The gas outlet from the reactor was fed to an MKS Cirrus bench-top residual gas analyzer, with mass signal m/z=28 (for nitrogen) monitored throughout the experiment.

Results and Discussion

X-ray diffractometry patterns were produced for each sample and compared to literature to identify their composition.

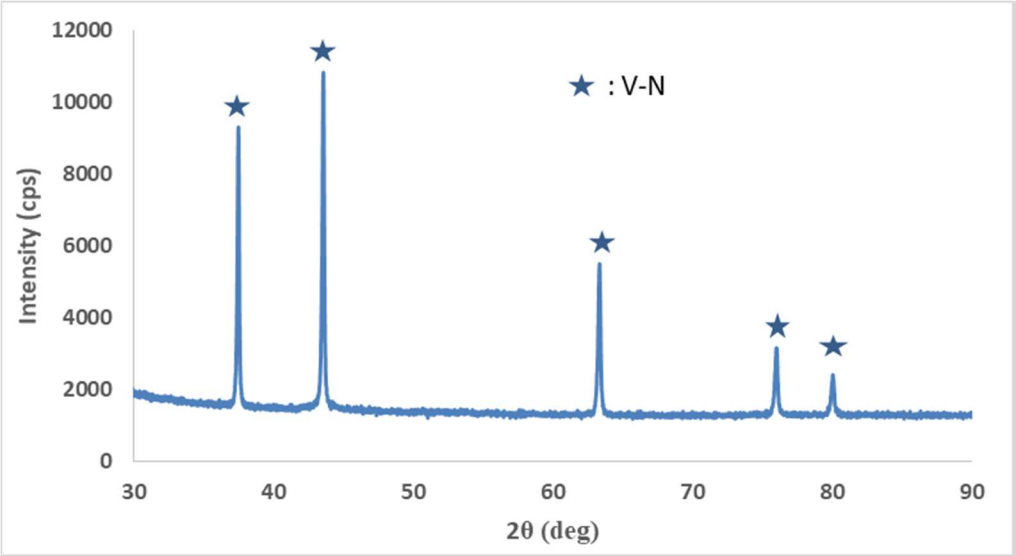

Figure 1: X-ray Diffractometry Pattern of Vanadium Nitride Sample

Figure 1 shows the results of the XRD performed on the vanadium nitride sample. Comparing the results with the XRD pattern from the study performed by Zhao et al., the peaks matched up exactly in position and relative intensity [4]. Since all of the apparent peaks are consistent with those for vanadium nitride, the synthesis of pure vanadium nitride was successful.

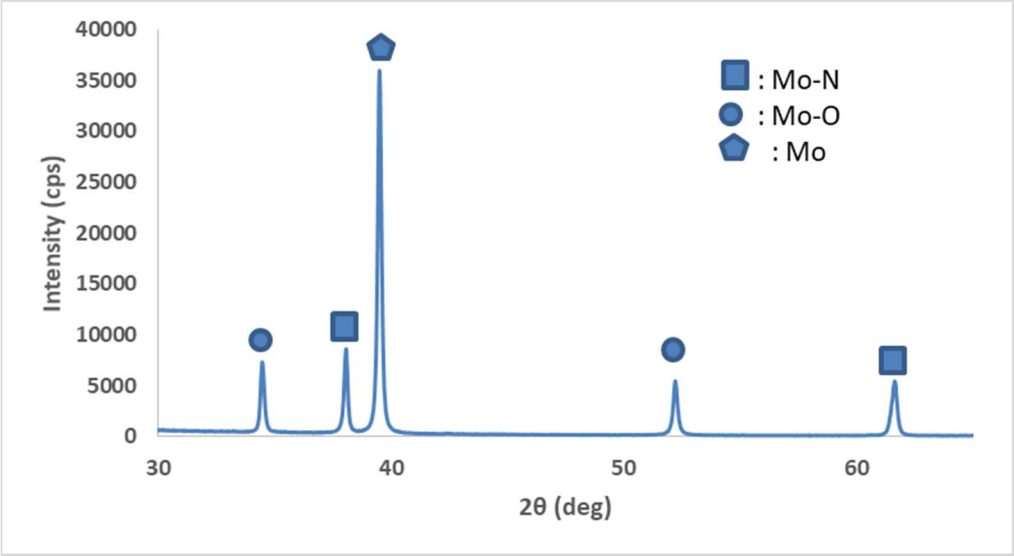

Figure 2: X-ray Diffractometry Pattern of Molybdenum Nitride Sample (1050 °C)

Figure 2 shows the results of the XRD performed on the molybdenum nitride sample nitrided at 1050 °C. The sample appears to be a mixture of Mo, Mo-O, and Mo-N [5]. While the sample does contain Mo-N, the relative intensities of Mo-N peaks to Mo peaks suggest that the material may be mostly Mo. Since the synthesis method for this sample was based on the V-N method, this could suggest why the synthesis seemed to have been unsuccessful. In order to investigate the effect of nitridation temperature, the molybdenum nitride sample was reproduced at a lower nitridation temperature of 950 °C.

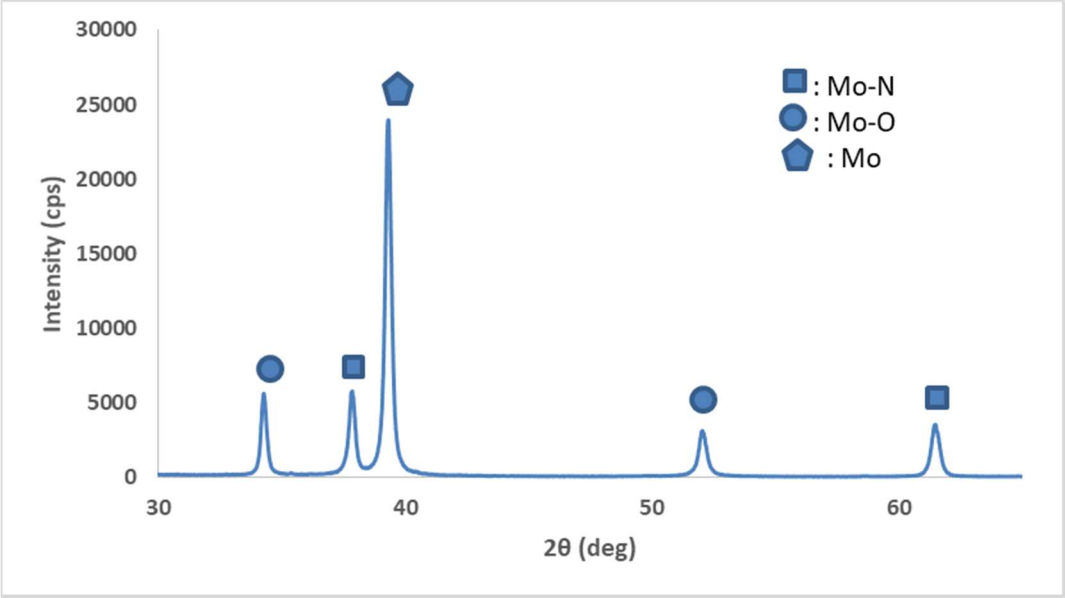

Figure 3: X-ray Diffractometry Pattern of Molybdenum Nitride Sample (950 °C)

Figure 3 shows the results of the XRD performed on the molybdenum nitride sample that was nitrided at 950 °C. The results show that the structure of this sample is similar to the one nitrided at 1050 °C. This could suggest that the nitridation temperature does not have a significant impact on the synthesis of the metal nitride beyond the minimum temperature required. The TPD study was performed on both to see if there were differences in the decomposition of the two samples.

In our preliminary study of iron nitride, we found that iron nitride was active in the production of ammonia. In order to determine if its stability is strong enough for operation in a SOFC-like reactor, the temperature-programmed decomposition analysis was performed on the iron nitride sample. In order to compare the new samples, the iron nitride provided a basis for the comparison.

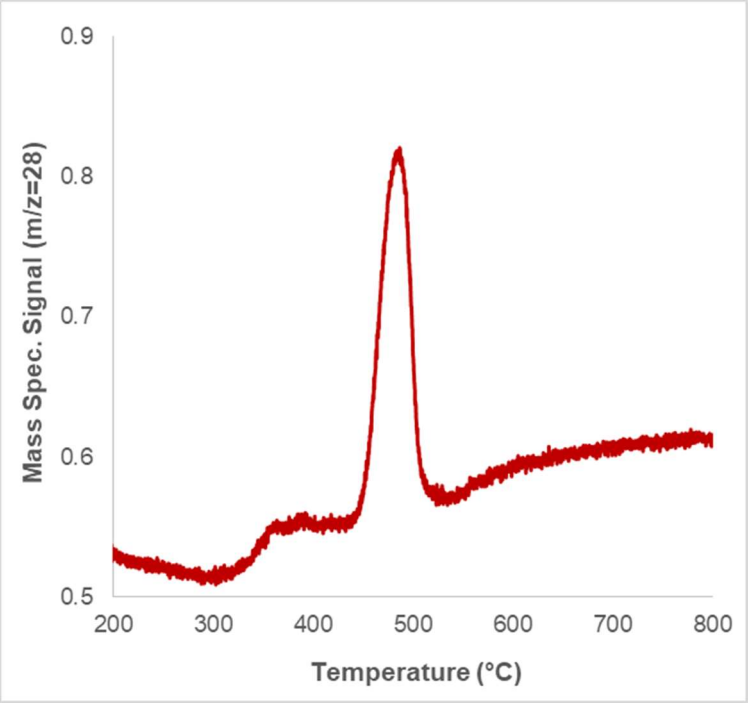

Figure 4: Iron (iii) Nitride Temperature-Programmed Decomposition

Figure 4 shows the TPD analysis performed on the iron (iii) nitride sample. Nitrogen gas began to come off the sample at a temperature of 360 °C and ended at 510 °C. This suggests that the material began to decompose at a temperature of 360 °C and was completely depleted of nitrogen at a temperature of 510 °C. This would not make it suitable for electro-catalytic ammonia production since target operating temperature of the SOFC-like reactor will be 700 °C.

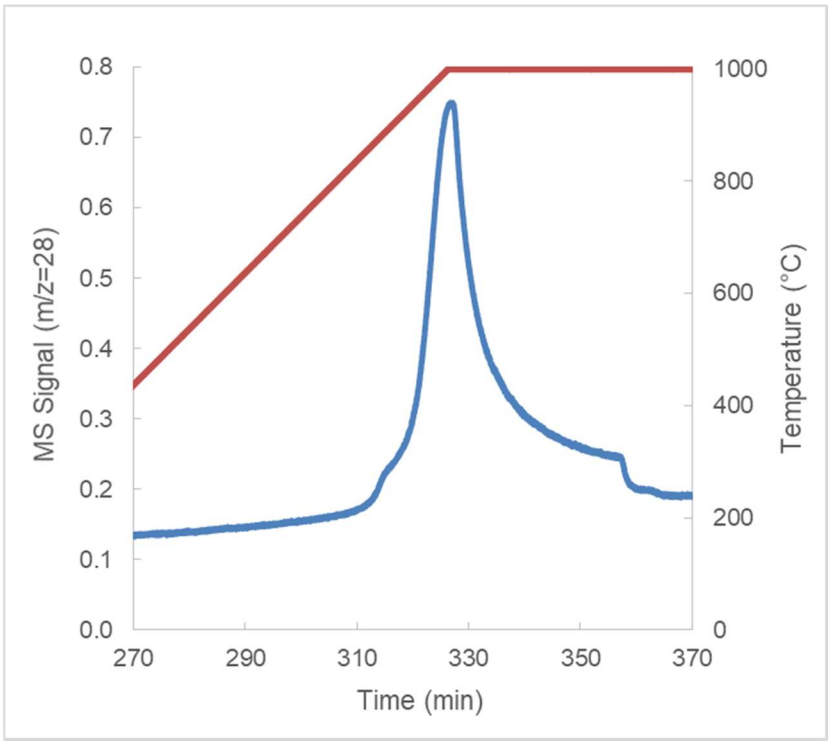

Figure 5: Vanadium Nitride Temperature-Programmed Decomposition

Figure 5 shows the TPD analysis performed on the vanadium nitride sample. Nitrogen gas began to appear in the outlet at about 900 °C and stopped at 40 minutes after reaching 1000 °C. This suggests that the vanadium nitride sample is stable up to temperatures of 900 °C. This would make vanadium nitride suitable for electro-catalytic ammonia production in the SOFC-like reactor.

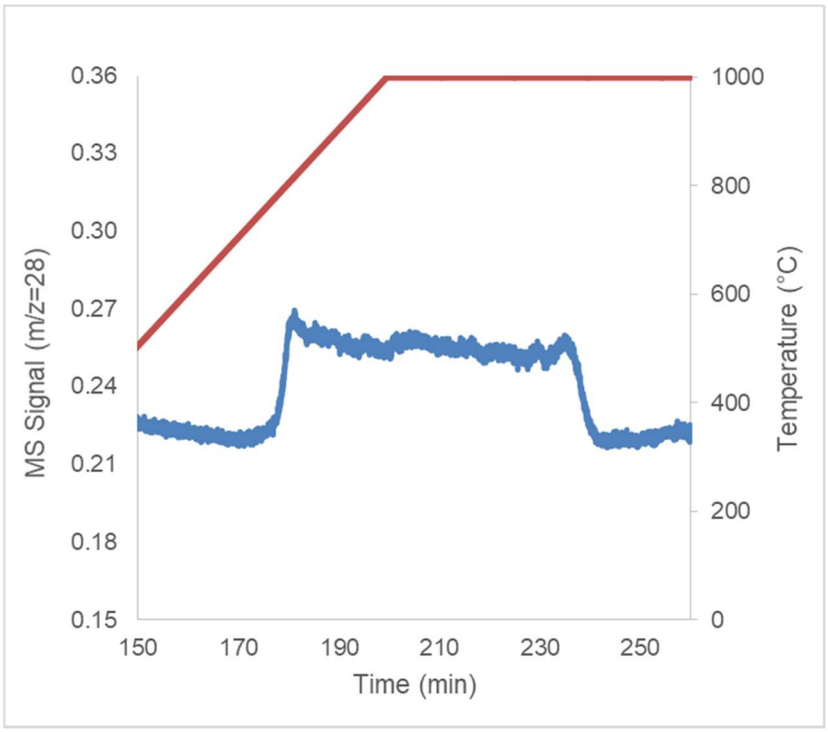

Figure 6: Molybdenum Nitride (1050 °C) Temperature-Programmed Decomposition

Figure 6 shows the TPD analysis performed on the molybdenum nitride sample nitrided at 1050 °C. Instead of a large peak in the center, the rate of nitrogen gas leaving the material seemed to plateau and last for a longer period of time than the vanadium sample. Nitrogen gas began to appear in the outlet at 800 °C and stopped 40 minutes after reaching 1000 °C. This could suggest that the molybdenum nitride sample is stable up to temperatures of 800 °C. However, since the sample's rate of decomposition seemed to plateau, this could suggest that something is wrong with the sample. If this TPD analysis is accurate of the Mo-N, then this would make molybdenum nitride suitable for electro-catalytic ammonia production in the SOFC-like reactor.

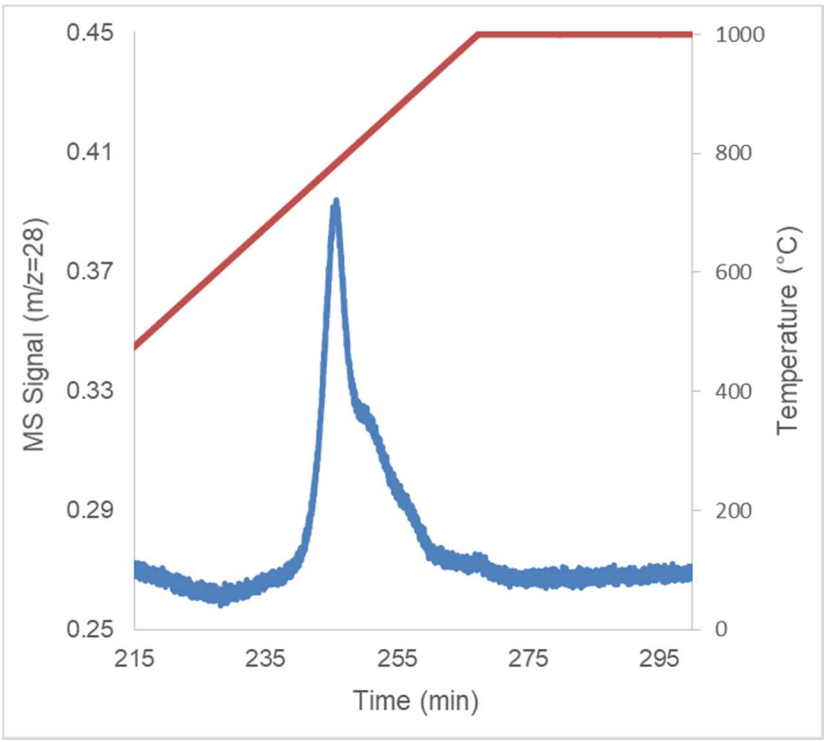

Figure 7: Molybdenum Nitride(950 °C) Temperature-Programmed Decomposition

Figure 7 shows the TPD analysis performed on the molybdenum nitride sample nitrided at 950 °C. Unlike the molybdenum sample nitrided at 1050 °C, this sample seemed to match the behavior of the vanadium and iron samples with a large peak. Nitrogen gas began to appear in the outlet at 730 °C and stopped after reaching 850 °C. This suggests that this molybdenum nitride sample is stable up to temperatures of 730 °C. If this TPD analysis is accurate of the MoN, then this would make molybdenum nitride suitable for electro-catalytic ammonia production in the SOFC-like reactor.

While both synthesis methods of vanadium nitride and molybdenum nitride were able to produce an amount of the target metal nitride, the vanadium nitride was considerably more pure. Decomposition temperatures of both samples seemed to make them suitable for application in an SOFC-like reactor. Interestingly, the synthesis temperature seemed to have an

effect on the decomposition rate of the two molybdenum nitride samples. However, there did not seem to be a difference in the XRD patterns for the two samples.

Conclusion

In the present study, vanadium nitride and molybdenum nitride type materials, which are potential candidates for atmospheric pressure ammonia production in an SOFC-type reactor, were synthesized and characterized. The XRD pattern of V-N showed that the final product is pure, however there were impurities in XRD pattern of Mo-N. Since the synthesis method appeared to be successful in producing pure vanadium nitride that was stable at temperatures above 700 °C, the vanadium nitride will be implemented in the SOFC-like reactor. Although molybdenum nitride appeared to be stable at temperatures above the target temperature, the synthesis was not pure. Further research into synthesis methods that will work need to be investigated and determine if they still produce the same stability as this study. In addition to these two metal nitrides, chromium nitride, zirconium nitride, and niobium nitride will be investigated as well. Once enough of the metal nitrides have been determined to be stable with a proper synthesis method for producing pure samples have been established, these metal nitrides will be implemented into SOFC-like reactors to analyze their abilities to produce ammonia at ambient pressure.

References

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